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(56) Documents Cited

GB 1575124 A GB 1300954 A GB 1278473 A
GB 0976617 A GB 0943488 A EP 0244133 A2
US 5944888 A US 5766686 A
WPI Accession no 74-01670V & JP480043779 B
WPI Accession no 72-73844T & JP470043723 B

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(54) Abstract Title

Investment casting

(57) A method of investment casting comprises the preparation of a refractory slurry by mixing a binder, a refractory material, and a quantity of water-insoluble organic fibres, and the application of one or more coats of this slurry to an expendable pattern, so as to build up a shell. It has been found that each coat of the slurry thus formed is surprisingly thick, and that a relatively short drying time is required for each coat, hence enabling a shell of desirable thickness to be rapidly built in a small number of "dipping cycles". A kit of ingredients for putting the method of the invention into effect; a shell produced in accordance with this method; and a refractory slurry for use in this method are also disclosed. The water-insoluble organic fibres may be formed of polypropylene.

IMPROVEMENTS IN AND RELATING TO INVESTMENT CASTING

5 The present invention relates to improvements in and relating to investment casting. In particular, the invention relates to a method of investment casting which involves the successive application of one or more coats of a refractory slurry to an expendable pattern, so as to build up a shell. The present invention further provides a refractory slurry for use in the method of the invention, and a kit of ingredients for putting the method of the
10 invention into effect.

The process of investment casting, otherwise known as the lost wax process, is well known and widely used. Typically, the process involves dipping a wax model into a slurry comprising a binder and a refractory material, so as
15 to coat the model with a layer of slurry; applying a stucco coating of dry refractory to the surface of the layer; allowing the resulting stuccoed slurry layer to dry; and applying further stuccoed slurry layers as appropriate to create a shell mould around the wax model having a suitable thickness. After thorough drying, the wax model is eliminated from the shell mould, and the
20 mould is fired.

Environmental considerations dictate that the binder used in the investment casting process should be water-based, rather than alcohol-based. Customarily, the binder used comprises an aqueous colloidal silica sol. When
25 combined with a suitable refractory material into a slurry, aqueous silica sols are capable of gelling and drying to form a green shape having an acceptable degree of green strength. However, the time taken for this process is disadvantageously long. A single stuccoed slurry layer, applied to a wax model in the course of investment casting, may take between 3-8 hours to
30 dry. Where the model comprises recessed parts or other complex

configurations, the drying time may be increased to 24 hours or more. During production of a shell mould having several stuccoed layers, this time must be multiplied by the number of coats applied. Typically, 4-8 coats are required in order to build a shell of acceptable thickness, thereby bringing
5 the total production time to the order of between 12 hours and several days.

Considerable effort has therefore been devoted in the prior art towards accelerating the coat drying time. Thus, for example, EP-A-0638379 discloses that the addition to a colloidal silica sol binder of an elastomeric
10 polymer, such as styrene butadiene, results in a significant reduction in the drying time and an improvement in green strength. The addition of soluble organic polymers to a colloidal silica sol binder for use in investment casting is also disclosed in US 4996084. Soluble organic polymers however readily "wet out", and it has been found that the green strength of a shell mould
15 comprising such polymers is temporarily reduced by the permeation of steam through the mould, for example during the elimination of the wax model from the mould. Moreover, soluble organic polymers are expensive, and their use in investment casting may significantly increase the cost of this process.

20 It remains therefore a desirable object to provide an alternative means for reducing the time required to build a shell mould of suitable thickness during the process of investment casting.

According to one aspect of the present invention, therefore, there is provided
25 a method of investment casting, comprising the steps of mixing a binder, a refractory material, and a quantity of water-insoluble organic fibres to form a slurry; coating an expendable pattern with a coat of said slurry; and drying said coat or allowing said coat to dry to form a shell. Optionally, a plurality of coats may be applied successively to said expendable pattern, each coat
30 being partly or wholly dried or allowed to dry prior to the application of the

next coat. Typically, between 2-10 coats, more preferably 3-8 coats, still more preferably 3, 4 or 5 coats, are successively applied to said pattern. In some embodiments, said expendable pattern is precoated in accordance with known conventional methods with a coat of slurry comprising no water-insoluble organic fibres, prior to the application in accordance with the present invention of one or more coats of fibre-modified slurry.

According to a further aspect of the present invention, there is provided a slurry comprising a binder, a refractory material and a quantity of water-insoluble organic fibres, which slurry is adapted for use in the method of the present invention.

According to yet another aspect of the present invention, there is provided a kit adapted for putting the method of the present invention into effect, said kit comprising a quantity of a binder, a quantity of a refractory material, and a quantity of water-insoluble organic fibres; said binder, refractory material and fibres being adapted to be mixed to form a slurry in accordance with the present invention.

Surprisingly, the present inventors have found that a refractory slurry comprising a quantity of water-insoluble organic fibres is capable of forming significantly thicker coats around dipped objects than are slurries of the types known in the prior art. An increase in coat thickness obviously implies a concomitant decrease in the number of dipping cycles required to build a mould of sufficient thickness, and hence a significant reduction in the rate of refractory mould production. Coats of fibre-modified slurry are subject to a diminished drying time in comparison with the products of the prior art, and have been found to possess a comparable green strength.

It has furthermore been found that the efficacy of elastomer-modified binders

of the kind disclosed in EP-A-0638379 and US 4996084 is largely destroyed by exposure of the binders to low temperatures (0°C and below). No such effect is in general observed with the fibre-modified refractory slurries and binders of the present invention, which may in most cases be safely exposed to low temperatures without adverse consequences. Moreover, in further contrast to the elastomer-modified compositions of the prior art, fibre-modified refractory slurries in accordance with the present invention have been found to be compatible with many types of antifreezes. This will therefore make possible the addition of antifreeze to binders intended for use in the fibre-modified slurries of the present invention, hence facilitating winter transport and storage of such binders.

Advantageously, said fibres are dispersed in said binder prior to the addition of said refractory material. This will promote the formation of a smooth and stable slurry. However, said refractory material may alternatively be added to said binder prior to the addition of said fibres.

Optionally, said expendable pattern may be coated with said slurry by means of pouring said slurry over the pattern. More preferably, however, said pattern may be coated by means of dipping the pattern into a receptacle containing said slurry. Conveniently, a plurality of patterns, which may for example be held on a "tree", may be dipped simultaneously into said receptacle, thereby enabling the simultaneous production of a plurality of shell moulds.

Advantageously, a plurality of coats of slurry may be applied successively to said expendable pattern. In accordance with usual practice, each coat of slurry may be stuccoed with a dry refractory material such as aluminosilicate (available from English China Clay under the Registered Trade Mark Molochite) or zircon sand prior to the application of the next coat.

Preferably, each coat of slurry may be completely covered with a layer of said dry refractory material prior to the application of the next coat.

5 Advantageously, said method may further include the step of eliminating said expendable pattern from said shell. Said expendable pattern may conveniently be eliminated by means of heating said shell to a temperature which exceeds the melting point of said pattern such that the pattern is caused to melt, and draining the pattern from the shell. Alternatively, said
10 pattern may be eliminated by means of heating said shell to a temperature which exceeds the sublimation or decomposition temperature of said pattern such that the pattern is caused to sublime or decompose, and causing or permitting the pattern to escape from the shell as a gas. As a further alternative, said pattern may be eliminated by dissolving the pattern in a suitable solvent and draining the resulting solution from the shell.

15 Where said pattern comprises a wax model, the wax may, for example, be eliminated from said shell by heating said shell in a wax autoclave, or by flash firing the wax.

20 Preferably, said fibres may be selected such that the step of eliminating said pattern from the shell does not cause the elimination of the fibres from the shell. Thus, where said pattern is to be eliminated by means of heating said shell to an elimination temperature which exceeds the melting point or sublimation temperature or decomposition temperature of said expendable
25 pattern, said fibres may be selected such that the melting point of said fibres exceeds said elimination temperature. This will ensure that the fibres remain intact notwithstanding elimination of the pattern. The retention of said fibres in the shell will serve to maintain the green strength of the shell.

30 Typically, the melting point of said fibres may be in the region of 150-

300°C, preferably 180-250°C, still more preferably 200-220°C. Such fibres may be particularly appropriate for use in conjunction with an expendable wax pattern.

- 5 The method of the present invention may further comprise the step of heating said shell to a firing temperature for firing the shell. Typically, said firing temperature may be in the range from 800°C to 1100°C.

10 Advantageously, said fibres may be selected such that the melting point of said fibres is lower than said firing temperature, such that said fibres are melted when the shell is fired. Accordingly, said fibres may be eliminated from the shell during or following firing. The elimination of said fibres from the shell will serve to create porosity in the shell, thereby making possible the escape of expanding gases from the interior of the shell during the
15 subsequent casting of molten metal therein; and hence reducing the likelihood that the shell will crack under internal gas pressure generated at this stage.

20 Said fibres may be spun and cut or milled in accordance with methods well known to the man skilled in the art. Each fibre may be less than 3mm in length, and/or greater than 0.5mm in length. Typically, each fibre will be between 0.5mm and 1.5mm in length. Advantageously, the diameter of each fibre may be sufficient to enable the creation of a porous structure in the shell following elimination of the fibres from the shell, so as to allow the
25 escape of gases from the interior of the shell during metal casting. Thus, said fibres may have a denier in the range 1.5-2.5; more preferably 1.8-2.1.

In some embodiments, said quantity of fibres constitutes less than 10% by weight of the slurry. Preferably, said quantity of fibres may constitute less
30 than 8%, more preferably less than 5% (for example, 4%, 3%, 2% or 1%),

or still more preferably less than 1% (for example 0.5% or less), by weight of said slurry. The quantity of fibres used will be a factor in determining the viscosity of the slurry; and hence may be selected in each case to attain a slurry viscosity appropriate for the specific use or application intended for the slurry in that case.

Said fibres may be selected such that the specific gravity of the fibres is equal to or close to the specific gravity of the binder, such that the fibres can be readily and evenly dispersed within said binder. Typically, the specific gravity of said fibres may be in the range 0.5-3, more preferably 0.5-1.5, still more preferably 1-1.5.

Optionally, said slurry may comprise further ingredients, for modifying or improving the properties of the slurry. For example, said slurry may comprise an antifoaming agent, such as dimethylpolysiloxane. Additionally or alternatively, said slurry may comprise elastomers and/or water-soluble polymers such as styrene butadiene. Said slurry may also comprise one or more wetting agents, such as bis(polyoxyethylene) 2-ethylhexylphosphate (commercially available under the Registered Trade Mark VICTAWET).

In particularly preferred embodiments, said binder comprises a colloidal silica sol. Said silica sol may be alkaline, and may for example have a pH in the range 9.3 - 10. Alternatively, said silica sol may be neutral or acidic. Said silica sol may comprise 10-50% wt silica, typically 20-30% wt silica. Suitable binders for this purpose are widely available commercially; for example FASTCOTE (Registered Trade Mark) available from Ransom and Randolph, or Clinosol 3105, available from Clinochem Limited. Optionally, further components such as phosphates may be included in said binder.

Said refractory may comprise aluminosilicates, magnesia, zircon, and/or

other refractory materials well-known to the man skilled in the art. Typically, the amount of refractory used may comprise 100-500%wt, more preferably 100-200%wt, still more preferably about 150%wt, of said binder.

- 5 Following is a description, by way of example only, of embodiments of the present invention and methods for putting the invention into effect.

Example 1

10

A slurry in accordance with the invention was produced from the following components:

Silica Sol Binder

15

An aqueous silica sol comprising 24% wt silica, having an specific gravity (relative density) of approximately 1.167 and a nominal particle size of 10 nm at a pH of 10.2, and 0.5% wt/wt antifoam. Proprietary binders such as FASTCOTE (Registered Trade Mark) sold by Ransom and Randolph, Remasol/Adbond (Registered Trade Mark), Ludox (Registered Trade Mark),

20

Clinosol 3105, or combinations of these, may also be used.

Refractory

-200 mesh molochite (calcined aluminosilicate, commercially available from English China Clays).

25

Water-insoluble organic fibres

Polypropylene fibres; 1.8 denier, 1mm length.

30

The slurry was produced as follows. 6.13kg of refractory was added with thorough mixing to 3.5 litres (4.08kg) of silica sol binder (3:2 wt/wt ratio of

refractory : binder). The resulting mix was stirred constantly for 24 hours to wet-out. 63g of fibres (18g/litre of binder) were then added under agitation to the mix, to produce a slurry. Following thorough agitation and dispersion, the viscosity of the slurry was tested using a Zahn 4 viscosity measuring cup (result: 10 seconds) and a B4 viscosity measuring cup (result: 30 seconds),
5 in accordance with standard methods.

The slurry was used in accordance with the method of the present invention to coat a plurality of wax test bars of the kind routinely employed in British
10 Standard test procedure BS 1902. Each bar comprised an oblong block of wax measuring approximately 20cm by 2.5cm by 0.7cm.

The bars were initially chemically cleaned, washed and dried in accordance with normal good practice, and were pre-coated with a refractory slurry
15 comprising a silica sol binder, a zircon sand refractory, and a water soluble polymer, but containing no insoluble organic fibres; stuccoed; and dried. Each bar was then dipped into the fibre-modified slurry described above, held for a period of 10 - 20 seconds, and removed. Each bar was immediately stuccoed with Molochite 30/80 mesh grain and then placed
20 under a fan for 1 hour for drying.

After drying, a second coat was applied to each bar. Each bar was re-dipped as described above, stuccoed with Molochite 16/30 mesh grain, and dried for one hour. Four further coats of slurry and Molochite 16/30 mesh grain were
25 subsequently applied to each bar in this manner, each coat being allowed a drying time of 1 hour. Thus, a total of six coats were applied to each bar within the course of an 8-hour working day.

The coated bars were allowed to dry thoroughly overnight. Thereafter, each
30 bar was placed in an autoclave at 7-9 bar pressure and 165-185 °C, such that

the wax was melted out to leave a refractory shell. The shells were found to have an average thickness of approximately 8mm; that is, about 20% greater than the average thickness of shells formed under identical conditions from slurries comprising soluble organic polymers, of the kind known in the prior art.

The permeability of the shells produced in accordance with the method described above was found to be comparable with that of shells available in the prior art. Moreover the strength per unit thickness of each shell produced as above was found to be at least equivalent to that of shells previously available; each shell having a green MOR (modulus of rupture) of approximately 3.5MPa or 502.8psi.

The drying time required for each coat of fibre-modified slurry was also comparable with drying times of elastomer-modified prior art slurries. It is noted that the rate of drying may be increased by the addition of magnesia grain, such as Lycal 93/12 or 30/80 calcined MgO, to the stucco.

Shells made in accordance with the method described above may be fired at 1000 - 1050 °C for approximately 1 hour, and will thereafter be ready for casting with metal.

CLAIMS

- 1 A method of investment casting, comprising the steps of mixing a
binder, a refractory material, and a quantity of water-insoluble organic fibres
5 to form a slurry; coating an expendable pattern with one or more coats of
said slurry; and drying said one or more coats or allowing said one or more
coats to dry to form a shell.
- 2 A method as claimed in claim 1, wherein said expendable pattern is
10 coated with between 2-10, preferably between 3-5, coats of said slurry.
- 3 A method as claimed in claim 1 or claim 2, further comprising the
step of stuccoing each coat with a layer of a dry refractory material before
the application of the next coat.
- 15 A method as claimed in any of claims 1-3, further comprising the
step of removing said expendable pattern from said shell, optionally by
heating said shell to a temperature exceeding the melting point, or
sublimation or decomposition temperature, of said pattern, such that the
20 pattern is caused to melt, sublime or decompose, and causing or allowing
said pattern to escape from the shell.
- 5 A method as claimed in any preceding claim, further comprising the
step of heating said shell to a firing temperature for firing said shell.
- 25 A method as claimed in claim 5, characterised in that the melting
point of said fibres is lower than said firing temperature, such that the fibres
are caused to melt during firing of said shell.
- 30 7 A method as claimed in any preceding claim, characterised in that the

melting point of said fibres exceeds the melting point or decomposition or sublimation temperature of said pattern.

8 A method as claimed in any preceding claim, wherein said fibres
5 have a denier in the range 1.5-2.5, preferably 1.8-2.1.

9 A method as claimed in any preceding claim, wherein the length of
said fibres is less than 3mm and/or greater than 0.5mm, preferably between
0.5-1mm.

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10 A method as claimed in any preceding claim, wherein the specific
gravity of said fibres is in the range 0.5-3, preferably in the range 1-1.5.

11 A method as claimed in any preceding claim, wherein said water-
15 insoluble organic fibres comprise polypropylene fibres.

12 A method as claimed in any preceding claim, characterised in that
said quantity of fibres constitutes less than 10%, preferably less than 5%,
still more preferably less than 1%, most preferably less than 0.5%, by weight
20 of said slurry.

13 A method as claimed in any preceding claim, further comprising the
step of incorporating in said slurry a quantity of elastomers and/or water-
soluble polymers.

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14 A method as claimed in any preceding claim, further comprising the
step of incorporating in said slurry a quantity of an antifoaming agent such
as dimethylpolysiloxane.

30 15 A method as claimed in any preceding claim, further comprising the

step of incorporating in said slurry a quantity of an antifreeze.

16 A method as claimed in any preceding claim, further comprising the step of incorporating in said slurry a quantity of one or more wetting agents.

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17 A method as claimed in any preceding claim, wherein said binder comprises a colloidal silica sol, preferably an alkaline silica sol.

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18 A method as claimed in any preceding claim, wherein said refractory comprises aluminosilicates, magnesia, zircon, and/or other refractory materials well-known to the man skilled in the art.

19 A method substantially as hereinbefore described.

15

20 A kit of ingredients for putting the method of any of claims 1-19 into effect, which kit comprises a binder, a refractory material, and a quantity of water-insoluble organic fibres.

20

21 A kit as claimed in claim 20, wherein said refractory material is mixed with said binder.

22 A kit as claimed in claim 20 or claim 21, wherein said fibres are dispersed in said binder.

25

23 A kit as claimed in any of claims 20-22, wherein said binder further comprises an antifreeze.

24 A kit as claimed in any of claims 20-23, wherein said binder further comprises an antifoaming agent such as dimethylpolysiloxane.

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25 A kit as claimed in any of claims 20-24, wherein said binder further comprises elastomers and/or water-soluble polymers such as styrene butadiene.

5 26 A kit as claimed in any of claims 20-25, wherein said binder further comprises one or more wetting agents, such as bis(polyoxyethylene) 2-ethylhexylphosphate.

27 A shell produced by the method of any of claims 1-19.

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28 A refractory slurry comprising a binder, a refractory material, and a quantity of water-insoluble organic fibres, for use in the method of any of claims 1-19.

Amendments to the claims have been filed as follows

- 1 A method of investment casting, comprising the steps of mixing a
binder, a refractory material, and a quantity of water-insoluble organic fibres
5 to form a slurry; coating an expendable pattern with one or more coats of
said slurry; and drying said one or more coats or allowing said one or more
coats to dry to form a shell.
- 2 A method as claimed in claim 1, wherein said expendable pattern is
10 coated with between 2-10 coats of said slurry.
- 3 A method as claimed in claim 1 or claim 2, further comprising the
step of stuccoing each coat with a layer of a dry refractory material before
the application of the next coat.
- 15 4 A method as claimed in any of claims 1-3, further comprising the
step of removing said expendable pattern from said shell, optionally by
heating said shell to a temperature exceeding the melting point, or
sublimation or decomposition temperature, of said pattern, such that the
20 pattern is caused to melt, sublime or decompose, and causing or allowing
said pattern to escape from the shell.
- 5 A method as claimed in any preceding claim, further comprising the
step of heating said shell to a firing temperature for firing said shell.
- 25 6 A method as claimed in claim 5, characterised in that the melting
point of said fibres is lower than said firing temperature, such that the fibres
are caused to melt during firing of said shell.
- 30 7 A method as claimed in any preceding claim, characterised in that the

melting point of said fibres exceeds the melting point or decomposition or sublimation temperature of said pattern.

8 A method as claimed in any preceding claim, wherein said fibres
5 have a denier in the range 1.5-2.5.

9 A method as claimed in any preceding claim, wherein the length of said fibres is less than 3mm and/or greater than 0.5mm.

10 10 A method as claimed in any preceding claim, wherein the specific gravity of said fibres is in the range 0.5-3.

11 A method as claimed in any preceding claim, wherein said water-insoluble organic fibres comprise polypropylene fibres.

15

12 A method as claimed in any preceding claim, characterised in that said quantity of fibres constitutes less than 10% by weight of said slurry.

13 A method as claimed in any preceding claim, further comprising the
20 step of incorporating in said slurry a quantity of elastomers and/or water-soluble polymers.

14 A method as claimed in any preceding claim, further comprising the step of incorporating in said slurry a quantity of an antifoaming agent.

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15 A method as claimed in any preceding claim, further comprising the step of incorporating in said slurry a quantity of an antifreeze.

16 A method as claimed in any preceding claim, further comprising the
30 step of incorporating in said slurry a quantity of one or more wetting agents.

17 A method as claimed in any preceding claim, wherein said binder comprises a colloidal silica sol.

5 18 A method as claimed in any preceding claim, wherein said refractory comprises aluminosilicates, magnesia, and/or zircon.

19 A method substantially as hereinbefore described with reference to the Examples.

10 20 A kit of ingredients for putting the method of any of claims 1-19 into effect, which kit comprises a binder, a refractory material, a quantity of water-insoluble organic fibres having a length less than 3mm, and an antifoaming agent.

15 21 A kit as claimed in claim 20, wherein said refractory material is mixed with said binder.

22 A kit as claimed in claim 20 or claim 21, wherein said fibres are dispersed in said binder.

20 23 A kit as claimed in any of claims 20-22, wherein said binder further comprises an antifreeze.

25 24 A kit as claimed in any of claims 20-23, wherein said binder further comprises elastomers and/or water-soluble polymers such as styrene butadiene latex.

30 25 A kit as claimed in any of claims 20-24, wherein said binder further comprises one or more wetting agents, such as bis(polyoxyethylene) 2-ethylhexylphosphate.

- 26 A shell produced by the method of any of claims 1-19.
- 27 A refractory slurry comprising a binder, a refractory material, a quantity of water-insoluble organic fibres having a length less than 3mm,
- 5 and an antifoaming agent, for use in the method of any of claims 1-19.



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Claims searched: 1-28

Examiner: Pete Beddoe
Date of search: 25 July 2000

Patents Act 1977 Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:
UK CI (Ed.R): B3F FDF; B3G; B5A (AB11, AT12P)
Int CI (Ed.7): B22C (1/00, 3/00, 1/18, 1/20, 1/22, 1/24, 1/26); B29C (41/08, 67/14)
Other: Online: WPI, EPODOC, JAPIO

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
X	GB 1575124 (FOSECO) see esp exs 1-3	20,28 at least
X	GB 1300954 (RESIL) see esp exs	20,28 at least
X	GB 1278473 (FOSECO) see esp exs	20,28 at least
X	GB 976617 (SANDVIKENS) see esp p3 lines 11-72	20,28 at least
X	GB 943488 (BEAN) see esp p10 lines 95-101	20,28 at least
X	EP 0244133 A2 (FOSECO) see esp p3 lines 10-25	20,28 at least
X	US 5944888 (NORTH AMERICAN) see esp exs & p5 lines 3-10	1,20,27,28 at least
X	US 5766686 (NORTH AMERICAN) see esp exs & p4 line 67 - p5 line 3	1,20,27,28 at least
X	WPI Accession no 74-01670V & JP 48043779 B (KAWAMATA) see abstract	20,28 at least

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
		E	Patent document published on or after, but with priority date earlier than, the filing date of this application.
&	Member of the same patent family		